



## Paired electrooxidation IV. Decarboxylation of sodium gluconate to D-arabinose

C-F. CHOU and T-C. CHOU\*

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan, ROC

(\*author for correspondence, fax: +886-6-2366836, e-mail: tcchou@mail.ncku.edu.tw)

Received 25 January 2002; accepted in revised form 9 April 2003

**Key words:** arabinose, decarboxylation, paired electrooxidation, sodium gluconate

### Abstract

A paired electrooxidative method has been developed to synthesize D-arabinose in a divided cell. D-arabinose is a material which has an important role in the production of vitamin B2 and DNA. Sodium gluconate was directly oxidized at the anode and indirectly oxidized in the catholyte by bubbling oxygen which was reduced to  $\text{H}_2\text{O}_2$  and  $\text{OH}^\bullet$  free radicals. In the catholyte, indirect oxidation of sodium gluconate was mediated by  $\text{Fe}^{3+}$  and  $\text{OH}^\bullet$  free radicals. The optimal current efficiencies for D-arabinose production in the anolyte and catholyte were found to be 88.37% and 39.12%, respectively, and the total current efficiency of the paired electrooxidation was 127.49%. The paired electrosynthesis of D-arabinose is more economical in terms of power consumption than electrosynthesis that employ a single anode or cathode as the working electrode. The influence of cathodic/anodic CV and  $I/E$  curves, redox mediators and the amount of charge passed were also examined.

### 1. Introduction

D-arabinose is a monosaccharide, which plays an important role in the synthesis of vitamin B2 and DNA. D-arabinose is traditionally prepared by degradation oxidation, in which the carbon chain length of sodium gluconate or its derivatives is reduced using hydrogen peroxide as an oxidant and ferric ions as a catalyst [1]. The most common method for the industrial production of D-arabinose is the chemical oxidation of sodium D-gluconate with sodium hypochlorite [2]. Meanwhile, the electrochemical oxidation of sodium gluconate to form D-arabinose has been extensively studied during the last decade and is a potential method for commercialization [3–10]. Several investigators have suggested the use of a high efficiency reactor using a multisectioned porous electrode for the synthesis of D-arabinose [7–9]. The electrochemical method has been carried out using cerium sulfate as a mediator to directly react electrochemically with sodium gluconate to form D-arabinose on a platinum electrode [11].

Although, the electrochemical syntheses of organic compounds in a single cell have been reported [12–15], only a single electrode was used as the working electrode. The paired electrolysis method uses both the anode and the cathode as working electrode, which can simultaneously both anodically/electrochemically oxidize organic compounds [13–20]. The use of a paired electrolysis system for the degradation oxidation of sodium gluconate to D-arabinose is interesting as both the anodic and cathodic reactions generate the same

product simultaneously from the sodium gluconate. It also has the advantage of decreasing energy consumption. However, paired electrooxidation of decarboxylation has never been previously reported.

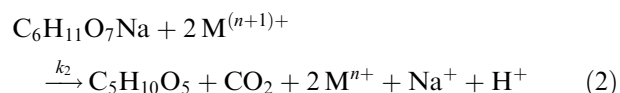
Based on the literature [13–20], the reactions representing the electrochemical oxidation of sodium gluconate to D-arabinose are as follows:

Anodic reaction

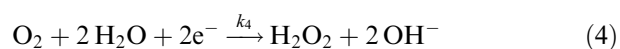


where  $\text{M}^{n+}/\text{M}^{(n+1)+}$  is the redox mediator in the anodic compartment.

Chemical reaction in the anodic compartment



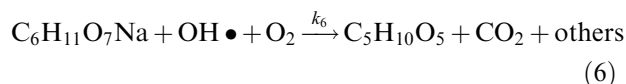
Cathodic reactions



where  $\text{R}^{(n-1)+}/\text{R}^{n+}$  is the redox mediator in the cathodic compartment.

Chemical reactions in the cathodic compartment





In this work, the paired electrooxidation of sodium gluconate to D-arabinose, using  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Cl}^-/\text{ClO}^-$  as mediators for the degradation oxidation of sodium gluconate in the anodic compartment and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{V}^{4+}/\text{V}^{5+}$  as mediators in the cathodic compartment, was studied and the factors affecting the current efficiency were also explored.

## 2. Experimental details

The paired electrolysis system includes an H-type divided glass cell and a d.c. power supply equipped with a potentiostat/galvanostat (EC&G model 273). The H-type divided glass cell was composed of a separated sintered glass frit (pyrex 4G) and two glass chambers accommodating the anolyte and catholyte, respectively, as shown in Figure 1. Both the anode and the cathode were made of graphite (area  $26.5 \text{ cm}^2$ ) and were used as working electrode. The reference electrode was Ag/AgCl in 3 M NaCl. The volume of the anolyte and catholyte was 100 ml in both the anodic and cathodic chambers. The anolyte and catholyte were kept well mixed by a magnetic stirrer. The anolyte and catholyte both contained 0.2 N  $\text{CH}_3\text{COOH}$  and 0.2 N  $\text{CH}_3\text{COONa}$  together with the desired concentrations of  $\text{FeCl}_3$  and aqueous sodium gluconate. Oxygen was bubbled through the catholyte at  $500 \text{ ml min}^{-1}$ .

During operation, samples from both the anolyte and the catholyte were periodically taken and analysed by high performance liquid chromatography (HPLC, model PU903 purchased from Jasco LC analyst). The chromatographic column was ICsep ICE-CORGEL 87H3. The column temperature was thermostatically controlled at  $70^\circ\text{C}$ . The flow rate of the  $1 \times 10^{-3} \text{ M}$   $\text{H}_2\text{SO}_4$  eluent solution was fixed at  $0.4 \text{ cm}^3 \text{ min}^{-1}$ . A refraction index (RI) detector was used. With the above operating

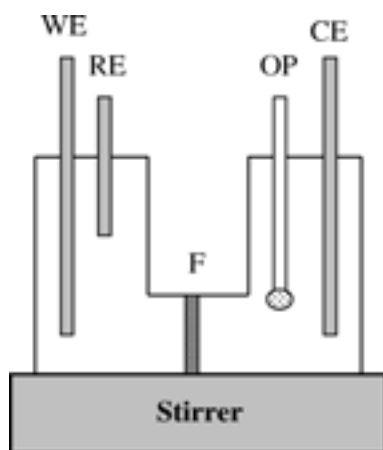


Fig. 1. Scheme of the cell: (WE) working electrode; (RE) reference electrode; (CE) counter electrode; (OP)  $\text{O}_2$  purge; (F) sintered glass filter (pyrex 4G).

conditions, the mean retention time was 15.1 min for sodium gluconate and 16.3 min for D-arabinose.

## 3. Results and discussion

### 3.1. CV and I/E curves of anodic oxidation

Figure 2 shows the of  $I/E$  curve with 0.12 M sodium gluconate and 0.2 N  $\text{CH}_3\text{COOH}$  and 0.2 N  $\text{CH}_3\text{COONa}$  solutions. The results revealed that the oxidation potential of sodium gluconate is approximately 1.08 V vs Ag/AgCl. The Tafel slope was approximately 168.2 mV as shown in the inset of Figure 2. Figure 3 shows the CV of the anodic oxidation of sodium gluconate and  $\text{FeCl}_3$ , respectively. The oxidation current at potentials larger than 1.08 V vs Ag/AgCl was greater than that without sodium gluconate. The oxidation potential of sodium gluconate was the same as that of the  $I/E$  curve as shown in Figure 2. Figure 3 also shows that the oxidation potential of  $\text{Fe}^{2+}$  when forming  $\text{Fe}^{3+}$  is 0.55 V vs Ag/AgCl and the reduction potential is  $-0.37 \text{ V}$  vs Ag/AgCl. Accordingly, the redox potential of  $\text{FeCl}_3$  is in the range  $-0.4$  to  $0.7 \text{ V}$  vs Ag/AgCl in the presence of  $\text{FeCl}_3$  which facilitates the oxidation of sodium gluconate. The results also showed that water was electrolysed to generate oxygen at the anode, while saturated oxygen was reduced to hydrogen peroxide and water at the cathode.

### 3.2. CV and I/E curves of the compounds in the cathodic chamber

Figure 4 shows the CV of sodium gluconate in the cathodic chamber. The reduction current generated with oxygen supplied to the cell at potentials lower than

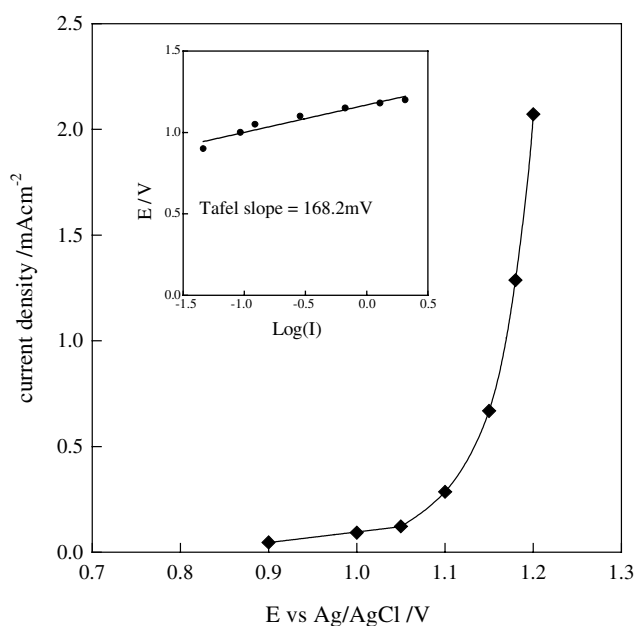


Fig. 2.  $I/E$  curves of sodium gluconate oxidation in the anodic cell. Working/counter electrode: graphite; reference electrode: Ag/AgCl; sodium gluconate concentration: 0.16 M; temperature:  $25^\circ\text{C}$ .

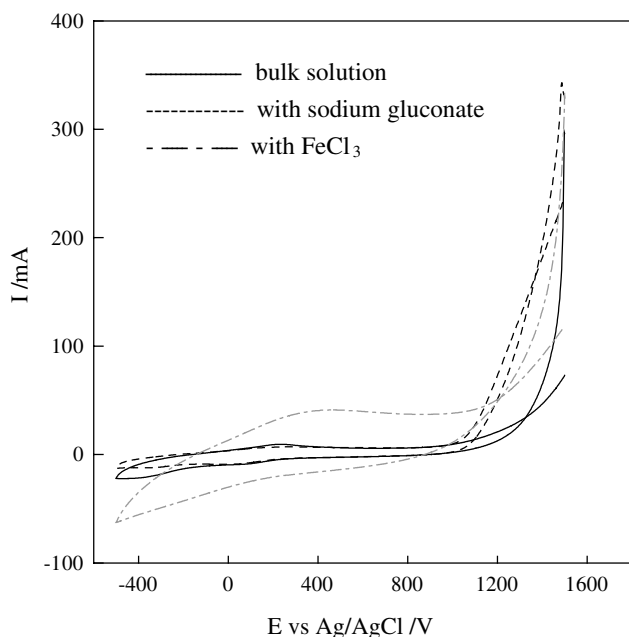


Fig. 3. Cyclic voltammogram for graphite electrode in 0.2 N  $\text{CH}_3\text{COOH}$  and 0.2 N  $\text{CH}_3\text{COONa}$  solution. Scanning rate  $20 \text{ mV min}^{-1}$ ,  $E_{\text{initial}} = +1.5 \text{ V}$ .

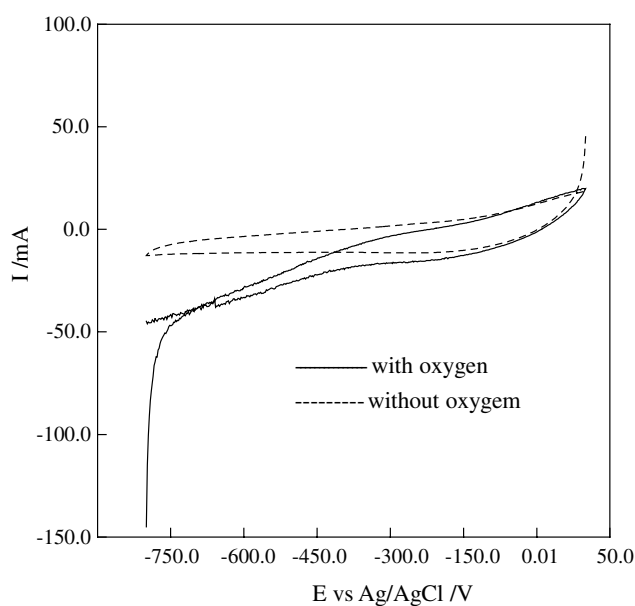
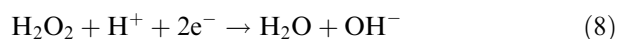
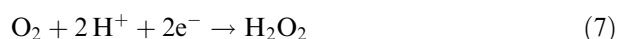


Fig. 4. Cyclic voltammogram for graphite electrode in 0.2 N  $\text{CH}_3\text{COOH}$  and 0.2 N  $\text{CH}_3\text{COONa}$  solution containing 0.07 M sodium gluconate. Scanning rate  $20 \text{ mV min}^{-1}$ ,  $E_{\text{initial}} = +100 \text{ mV}$ .

$-100 \text{ mV vs Ag/AgCl}$  is larger than that without oxygen. Based on [13–20], the cathodic reactions were



Obviously, the current results from the reduction of oxygen to varying extents as shown in Equations 7–9.

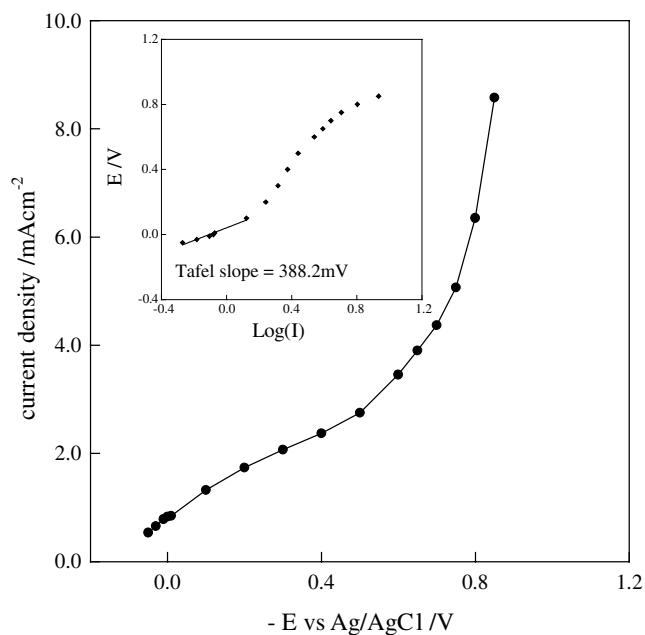


Fig. 5.  $I/E$  curves of sodium gluconate oxidation in the cathodic cell. Working/counter electrode: graphite; reference electrode:  $\text{Ag/AgCl}$ ; sodium gluconate concentration: 0.7 M; mediator: 0.05 M  $\text{FeCl}_3$ ; temperature:  $25^\circ\text{C}$ .

Within the two electron pathway  $\text{H}_2\text{O}_2$  and  $\text{OH}^\bullet$  free radicals form allowing sodium gluconate to be oxidized indirectly in the cathodic chamber.

As shown in Figure 5, the current associated with oxygen reduction increased whenever the cathodic potential was more negative than  $-0.2 \text{ V vs Ag/AgCl}$ . The limiting current density was  $2.75 \text{ mA cm}^{-2}$  when the cathodic potential was  $-0.5 \text{ V vs Ag/AgCl}$ . The side reaction at the cathode was the cathodic reaction of  $\text{H}_2\text{O}_2$  to form  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , which has been confirmed by the experimental data as shown in Figure 5. The Tafel slope of oxygen reduction was approximately  $-388.2 \text{ mV}$  as shown in Figure 5.

### 3.3. Current efficiency of the anodic oxidation of sodium gluconate

Two kinds of mediators were used to compare the current efficiency (CE) of the anodic degradation oxidation as shown in Table 1. The  $\text{OCl}^-$  ion is known to be a strong oxidant; this ion was able to further react with sodium gluconate to produce D-arabinose [2]. The  $\text{Cl}^-$  anion could be anodically oxidized to  $\text{OCl}^-$  at  $0.75 \text{ V vs SCE}$  [17, 21]. The optimal current efficiency for producing D-arabinose in the anodic chamber was 58.53% at 390 mM  $\text{NaCl}$ , 60 mM sodium gluconate,  $25^\circ\text{C}$  and  $1.32 \text{ mA cm}^{-2}$  current density as shown in Table 1.

When  $\text{Fe}^{3+}$  was used as a mediator and the  $\text{FeCl}_3$  concentration was increased from 0 to 59.8 mM, the current efficiency associated with the production of D-arabinose in the anodic chamber decreased from 85.98 to 11.63%. At higher concentration of  $\text{Fe}^{3+}$  ion lower

**Table 1.** Effect of anodic mediator on the arabinose production  
Working/counter electrode: graphite; sodium gluconate concentration: 60 mM; electrolyte solution: 0.2 N CH<sub>3</sub>COOH and 0.2 N CH<sub>3</sub>COONa solution; reference electrode: Ag/AgCl; charge passed: 0.55 F mol<sup>-1</sup> sodium gluconate; agitation rate: 600 rpm; temperature: 25 °C.

FeCl <sub>3</sub> /mM	NaCl /mM	Conc. of arabinose /mM	CE of arabinose /%
0	0	14.257	85.98
9.893	0	9.156	55.22
29.700	0	5.507	33.21
59.800	0	1.928	11.63
0	390.0	9.700	58.53

current efficiency was obtained. Thus, the current efficiency cannot be increased by using Fe<sup>3+</sup> as a mediator.

The results showed that the use of NaCl as a mediator to produce D-arabinose was better than FeCl<sub>3</sub>. When the Cl<sup>-</sup> ion or Fe<sup>3+</sup> ion was added, the current efficiency was still lower than that obtained by direct oxidation of sodium gluconate at the anode. Therefore, it is reasonable to conclude that a higher current efficiency can be achieved with no mediator present in the anodic oxidation of sodium gluconate.

### 3.4. Current efficiency of the sodium gluconate oxidation in cathodic chamber

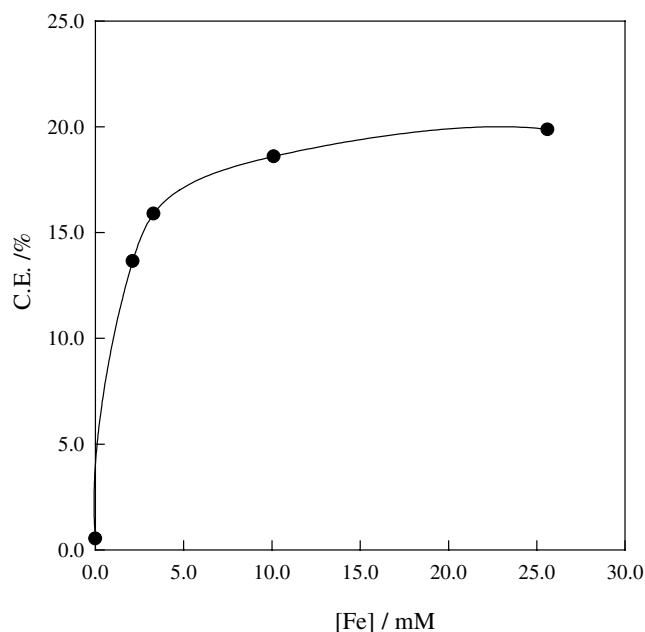
To produce a strong oxidant such as the OH• free radical in the catholyte, the use of redox mediators such as V<sup>4+</sup>/V<sup>5+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup> has been reported [13–20]. In this study, four kinds of redox mediators including NaVO<sub>3</sub>, FeCl<sub>3</sub>, Fe(OCH<sub>2</sub>CO)<sub>2</sub> and CeCl<sub>3</sub> were employed for the indirect oxidation of sodium gluconate in the cathodic chamber as shown in Table 2. The results indicated that the mediator couple Fe<sup>2+</sup>/Fe<sup>3+</sup> enhanced current efficiency relative to V<sup>4+</sup>/V<sup>5+</sup> and Ce<sup>3+</sup>/Ce<sup>4+</sup> at 60 mM sodium gluconate, 25 °C with a current density of 1.32 mA cm<sup>-2</sup>. Therefore FeCl<sub>3</sub> was chosen as the mediator giving the best current efficiency.

Increasing the Fe<sup>3+</sup> ion concentration from 0.0893 to 25.6 mM, increased the current efficiency from 0.54 to 19.88%, as shown in Figure 6. The Fe<sup>3+</sup> ion is appa-

**Table 2.** Comparison of different cathodic mediators on the arabinose production

Working/counter electrode: graphite; sodium gluconate concentration: 60 mM; electrolyte solution: 0.2 N CH<sub>3</sub>COOH and 0.2 N CH<sub>3</sub>COONa solution; reference electrode: Ag/AgCl; charge passed: 0.55 F mol<sup>-1</sup> sodium gluconate; agitation rate: 600 rpm; temperature: 25 °C.

Mediator	NaVO <sub>3</sub>	FeCl <sub>3</sub>	Fe(OCH <sub>2</sub> CO) <sub>2</sub>	CeCl <sub>3</sub>
Conc. of arabinose /mM	2.920	3.079	2.447	0.001
CE /%	14.763	18.571	17.61	0



**Fig. 6.** Effect of Fe<sup>3+</sup> concentration on the cathodic current efficiency of arabinose production. Working/counter electrode: graphite; sodium gluconate concentration: 60 mM; electrolyte solution: 0.2 N CH<sub>3</sub>COOH and 0.2 N CH<sub>3</sub>COONa solution; charge passed: 0.55 faraday mol<sup>-1</sup> sodium gluconate; agitation rate: 600 rpm; temperature: 25 °C.

rently promoting degradation oxidation in the cathodic chamber.

The current efficiencies for the oxidation of anthracene to anthraquinone and butanol to butyric acid in the cathodic chamber were very high [15, 16]. But it was not satisfactory within this protocol to oxidatively decarboxylate sodium gluconate in the cathodic chamber. The hydrogen peroxide forms a strong oxidant OH•, which oxidizes sodium gluconate. In a complicated manner leading to a significant amount of organic compounds being produced in the cathodic chamber. These byproducts were not identified. The oxidation occurring in cathodic chamber prefers the one-electron pathway rather than the two-electron pathway of decarboxylation. The Tafel slopes of the anodic and cathodic *I/E* curves are shown in Figures 2 and 5.

### 3.5. Overall pair degradation oxidation of sodium gluconate

By combining the oxidations in the cathodic and anodic chambers, the total arabinose production and current efficiency were obtained as shown in Table 3. Increasing the charge passed from 68.22 to 736.80 C decreased the current efficiency from 127.49 to 97.66%. The three curves of Figure 7 indicate that the results of the three different electrolysis styles of the two types of the single electrode as working electrode and the paired electrode as working electrode, were quite different. Obviously, the current efficiency obtained using the paired electrolysis was better than that found by using only an individual anode or cathode as the working electrode.

Table 3. Total current efficiency of the paired electrolysis of arabinose production

Working/counter electrode: graphite; sodium gluconate concentration: 60 mM; electrolyte solution: 0.2 N  $\text{CH}_3\text{COOH}$  and 0.2 N  $\text{CH}_3\text{COONa}$  solution; cathodic mediator: 0.05 M  $\text{FeCl}_3$ ; reference electrode: Ag/AgCl; current density:  $1.132 \text{ mA cm}^{-2}$ ; agitation rate: 600 rpm; temperature: 25 °C.

Charge passed /C	Cathode		Anode		Total CE /%
	Conc. of arabinose /mM	CE /%	Conc. of arabinose /mM	CE /%	
68.22	1.383	39.12	3.471	88.37	127.49
173.6	2.273	24.73	9.866	86.96	111.69
436.5	4.140	18.30	9.057	84.26	102.56
736.8	5.753	15.1	31.520	82.56	97.66

#### 4. Conclusions

The maximum current efficiency for the paired electro-oxidation of sodium gluconate to D-arabinose was 127.49% with a charge of 68.22 C being passed. The best current efficiency for anodic oxidation was 85% in this system using a single anode as the working electrode. The mediator  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in the catholyte generates the best current efficiency with the maximum value being 20% in the cathodic system. The current efficiency for the electrochemically oxidative decarboxylation of sodium gluconate to D-arabinose in the cathodic chamber was unsatisfactory. Paired electrooxidative decarboxylation is a new technology which, from the above results, shows a potential for commercialization.

#### Acknowledgements

The support of the National Yunlin University of Science and Technology of the Republic of China is acknowledged.

#### References

1. R. Wolf, Merck GmbH, *German Patents* 29 23 267 (1980) and 29 23 268 (1980), *Eur. Pat. Appl.* 20 959 (1981).
2. H.C. Fletcher, H.W. Dichl and C.S. Hudson, *J. Am. Chem. Soc.* **72** (1950) 4546.
3. *Japanese patents* 58-39 695 (1983) and 56-013 613 (1981).
4. G.W. Hay and F. Smith, *Can. J. Chem.* **47** (1969) 417.
5. J. Kubala, S. Kucar and K. Linek, *Czechoslovak Patent* 22 576 (1982).
6. Jiricay et al. *US Patent* 49 50 366 (1990).
7. F. Pergola, L. Nucci, G. Pezzatini, H. Wei and R. Guidelli, *Electrochim. Acta* **39** (1994) 1415.
8. G. Pezzatini, He Wei, R. Guidelli and F. Pergola, *Electroanal.* **4** (1992) 129.
9. C. Valliers and M. Matlosz, *J. Electrochem. Soc.* **146** (1999) 2399.
10. R.M. Moriarty and H.B. Ill, *Tetrahedron Lett.* **36** (1995) 9265.
11. *J. A Patents* 58 039 695A (1992).
12. S. Ito, M. Iwata and K. Sasaki, *Tetrahedron* **47** (1991) 841.
13. T.C. Chou, S.J. Liaw and B.J. Hwang, *J. Chin. Chem. Soc.* **34** (1987) 141.
14. J.J. Jow, A.C. Lee and T.C. Chou, *J. Appl. Electrochem.* **17** (1987) 753.
15. A.C. Lee and T.C. Chou, *J. Appl. Electrochem.* **23** (1993) 1259.
16. Y.L. Chen and T.C. Chou, *J. Appl. Electrochem.* **26** (1996) 543.
17. M.L. Tsai and T.C. Chou, *Ind. Eng. Chem. Res.* **36** (1997) 3563.
18. T.C. Chou and J.J. Jow, *ROC Patent* 67 036 (1994).
19. T.C. Chou, J.J. Jow and A.C. Lee, *ROC Patent* 30 226 (1988).
20. T.C. Chou and A.C. Lee, *US Patent* 5 466 346 (1995).
21. L.I. Krishtalik, *Electrochim. Acta* **26** (1981) 329.